

Polyelectrolyte Networks: Elasticity, Swelling, and the Violation of the Flory - Rehner Hypothesis *

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This paper discusses the elastic behavior of polyelectrolyte networks. The deformation behavior of single polyelectrolyte chains is discussed. It is shown that a strong coupling between interactions and chain elasticity exists. The theory of the complete crosslinked networks shows that the Flory - Rehner - Hypothesis (FRH) does not hold. The modulus contains contributions from the classical rubber elasticity and from the electrostatic interactions. The equilibrium degree of swelling is estimated by the assumption of a c^* -network.

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I. INTRODUCTION

The elastic behavior of polyelectrolyte networks is not understood. The main reason is the lack of knowledge in the interplay between the elastic part F_{el} of the free energy and the part from the interactions F_{int} . The simplest approximation to overcome this problem is the application of the Flory - Rehner - Hypothesis (FRH) which suggests that both parts of the free energy can be added [1]. Therefore the thermodynamic behavior of the network is then determined by the minimum of the total free energy $F = F_{el} + F_{int}$. This procedure must be wrong in general as pointed out by Ball and Edwards [2]. The first reason is purely energetic. If the partition function is formulated by using the Edwards technique (see [3] for a review), it must be expected that a cross term between both contributions exists. On the other hand it was shown recently that for realistic networks with fractal structural units, "left overs" from the network formation processes yield immediately a violation of the FR - hypothesis [4]. These results have been shown by analytical considerations and by numerical simulations.

Clearly the violation of the FRH was here shown to have purely structural reasons and it can be argued that for perfect networks the FRH should hold, as it was believed to be confirmed by many experimental work [5,6] on neutral networks and conventional rubbers upon swelling experiments. Indeed it is difficult to say anything on the validity of the FRH in swelling of conventional rubbers. Real rubber samples cannot be characterized as they should be and only indirect measurements such as neutron scattering [7] can give some hints, but the conclusions in favor or against the FRH seem to be vague. For a clear statement on the validity of the FRH, classical rubbers suffer from the fact that the interactions in these systems are weak. The interactions are "only" excluded volume forces and the corresponding potential is very short ranged. The short ranged excluded volume potential means that Flory Huggins type, or Random Phase Approximations (see for example [8,11]) work very well. However, the excluded volume interactions are weak and thus their effect on the elastic properties is indeed difficult to study with swelling experiments only.

Polyelectrolyte networks do not suffer from the lack of weak interactions. Moreover the range of the interaction can be changed during experiments. Very often the interaction between chain segments are described by a Debye - Hückel potential of the form $V(r) \propto 1/r \exp(-\kappa r)$, where r is the spatial distance between two segments and κ the Debye screening parameter, which depends mainly on the total ionization I [8-10], i.e., $\kappa^2 \propto I$. The latter means that the total ionization can be changed easily by adding and removing salt to / from the solution. The range and the effect of the interactions can be changed easily. Large ionization I corresponds a high concentration of salt and thus to large values of κ . In this case the interaction potential can be safely modeled by a short ranged form, in some sense with an excluded volume type potential with a certain value determined by the Bjerrum length and κ [12]. The more interesting case is therefore the regime of small values of the Debye screening parameter corresponding to long range potentials. This is the regime discussed below in more detail.

*Dedicated to Bruce Eichinger. The authors consider it a great honor to be invited to contribute to the special issue for Bruce Eichinger.

We will show below systematically that the FRH is not applicable to the case of polyelectrolyte networks. To do so we first derivate the Flory-Rehner Hypothesis. Then to make the paper self contained we start with the computation of the deformation of a single polyelectrolyte chain, though some progress has already been achieved [13] by the application of blob-pictures [14]. Indeed these ideas have been also applied to networks [13]. The problem is here is that the such obtained results are based on single chain approaches. Therefore these results are restricted to cases where either the meshes are largely stretched, or the electrostatic interactions are screened. These two cases are reflected on the ratio of the screening length and the chain size, i.e., $1/\kappa$ much larger than the mean mesh size radius the network or vice versa. In the latter the network behaves almost as a classical swollen network, whereas the first case corresponds to the strong polyelectrolyte regime [13]. In the present paper we will also present a theory beyond these two extreme regimes. Moreover we will leave in the following the single mesh approximation and study a network composed by many meshes. Then we cannot rely on the extreme cases κ large or small.

Our results will show that there is a strong interplay between the elastic force and the interactions. The force extension relationship is in contrast to neutral Gaussian chains not only dependent on the chain length and temperature [15] but also a strong effect on the single chain modulus from the electrostatic interaction appears [16]. This method will be generalized to polyelectrolyte networks [17]. We show below that the elastic modulus is a combination of both contributions, i.e., the classical elastic part, determined by crosslinks only [18] and a new part coming from the interactions. Thus the modulus is determined strongly by the strength and the range of the interaction. Note that this is not the case for neutral networks. All computations for excluded volume networks so far show, that the modulus is determined by the number of crosslinks only [18,19]. In the third main part of the paper we use the single chain results to study the swelling behavior of polyelectrolyte networks. Before we proceed we present a mathematical formulation of the origin of the FRH to show what has to be done to go beyond the classical theories.

II. DERIVATION AND LIMITS OF THE FLORY-REHNER-HYPOTHESIS

We consider a polyelectrolyte network in solvent containing N_i indistinguishable counter-ions. The partition function for such a network consisting of one very long single chain with a fixed crosslink-configuration \mathbf{S} in terms of a path integral reads:

$$Z(\mathbf{S}) = \frac{1}{N_i!} \int \mathcal{D}\mathbf{r}(s) \int \frac{d\mathbf{R}_1}{V_0} \dots \int \frac{d\mathbf{R}_{N_i}}{V_0} \exp(-\beta H) \prod_{(i,j)} \delta[\mathbf{r}(s_i) - \mathbf{r}(s_j)], \quad (1)$$

here (i,j) denotes that the i -th and the j -th monomer form a crosslink, $\mathbf{r}(s)$ represents the chain conformation in three dimensions as a function of the contour variable s and \mathbf{R}_l is the position of the l -th counterion. V_0 denotes the integration-volume. As we assume that the network is weakly charged the underlying Hamiltonian H is given by an Edwards Hamiltonian for flexible chains. Considering the counterions explicitly the Hamiltonian H is:

$$\begin{aligned} \beta H = & \frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 + \frac{\beta}{2} \int_0^{N_0} ds \int_0^{N_0} ds' \frac{z^2}{4\pi\epsilon_0\epsilon_r |\mathbf{r}(s) - \mathbf{r}(s')|} \\ & + \beta \sum_{i=1}^{N_i} \int_0^{N_0} ds \frac{zz_i}{4\pi\epsilon_0\epsilon_r |\mathbf{r}(s) - \mathbf{R}_i|} + \frac{\beta}{2} \sum_{i,l=1}^{N_i} \frac{z_i z_l}{4\pi\epsilon_0\epsilon_r |\mathbf{R}_i - \mathbf{R}_l|} \end{aligned} \quad (2)$$

where l is the Kuhn length, N_0 the total number of monomers of the crosslinked chain, β is $(k_B T)^{-1}$, where k_B is the Boltzmann constant and T denotes the absolute temperature. ϵ_0 is the dielectric constant and ϵ_r the relative dielectric constant. z is the monomer charge in units of e and z_i is charge of the i -th counterion, which is assumed to be independent of i . \mathbf{R}_i denotes the position of the i -th counterion.

In order to use collective coordinates, we introduce the densities ρ_p of the polymers and ρ_i for the counterions. The constrained partition function for fixed densities ρ_p and ρ_i reads (see Appendix A):

$$\begin{aligned} Z(\rho_p, \rho_i, \mathbf{S}) = & \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \left(\frac{1}{\tilde{S}_0(\mathbf{k})} + V_{pp}(\mathbf{k}) \right) \rho_p(\mathbf{k}) \rho_p(-\mathbf{k}) \right] \\ & \times \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \left(\frac{1}{C_0(\mathbf{k})} + V_{ii}(\mathbf{k}) \right) \rho_i(\mathbf{k}) \rho_i(-\mathbf{k}) - \sum_{\mathbf{k}} V_{pi}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_i(-\mathbf{k}) \right] \end{aligned} \quad (3)$$

with $V_{pp}(\mathbf{k}) = bz^2/\mathbf{k}^2$. V_{pi} and V_{ii} are defined analogously. $\tilde{S}_0(\mathbf{k})$ and $C_0(\mathbf{k})$ are defined as:

$$\tilde{S}_0(\mathbf{k}) = \left\langle \int_0^{N_0} ds \int_0^{N_0} ds' e^{i\mathbf{k}(\mathbf{r}(s) - \mathbf{r}(s'))} \right\rangle_0 \quad (4)$$

and

$$C_0(\mathbf{k}) = \left\langle \sum_{j,l=1}^{N_i} e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_l)} \right\rangle_0 \quad (5)$$

where $\langle \dots \rangle_0$ means the expectation value with respect to H_0 :

$$\beta H_0 = \frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 + \ln \left(\prod_{(i,j)} \delta[\mathbf{r}(s_i) - \mathbf{r}(s_j)] \right) \quad (6)$$

Eq. (3) defines an effective Hamiltonian H_{eff} :

$$\begin{aligned} \beta H_{\text{eff}}(\rho_p, \rho_i) = & \frac{1}{2} \sum_{\mathbf{k}} \left(\frac{1}{\tilde{S}_0(\mathbf{k})} + V_{\text{pp}}(\mathbf{k}) \right) \rho_p(\mathbf{k}) \rho_p(-\mathbf{k}) + \frac{1}{2} \sum_{\mathbf{k}} \left(\frac{1}{C_0(\mathbf{k})} + V_{\text{ii}}(\mathbf{k}) \right) \rho_i(\mathbf{k}) \rho_i(-\mathbf{k}) \\ & + \sum_{\mathbf{k}} V_{\text{pi}}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_i(-\mathbf{k}) \end{aligned} \quad (7)$$

From the effective Hamiltonian we separate the $\mathbf{k} = 0$ term, i.e.:

$$\beta H_{\text{eff}} = \beta H_{\text{eff}}^0(\rho_p(0), \rho_i(0)) + \sum_{k>0} \beta H'_{\text{eff}}(\rho_p(\mathbf{k}), \rho_i(\mathbf{k})) \quad (8)$$

with

$$\begin{aligned} \beta H_{\text{eff}}^0(\rho_p(0), \rho_i(0)) = & \frac{1}{2} \left(\frac{1}{\tilde{S}_0(0)} + V_{\text{pp}}(0) \right) \rho_p(0) \rho_p(0) + \frac{1}{2} \left(\frac{1}{C_0(0)} + V_{\text{ii}}(0) \right) \rho_i(0) \rho_i(0) \\ & + V_{\text{pi}}(0) \rho_p(0) \rho_i(0) \end{aligned} \quad (9)$$

For pure Coulomb potentials in infinite large systems the values for $V_{\text{pp}}(0)$, $V_{\text{pi}}(0)$ and $V_{\text{ii}}(0)$ appear to be divergent. In realistic systems the chains (and meshsizes) are finite. The lowest value for the wave vector is then of the order of $|\mathbf{k}^2| \sim 1/(l^2 N_0)$ which acts as a cut off for small wave vectors. Thus divergences are prevented.

If fluctuations are neglected the only contribution to the partition function stems from H_{eff}^0 . In this case the Free Energy F_0 reads:

$$\begin{aligned} F_0 = & -\ln(Z_0(\rho_p(0), \rho_i(0))) \\ = & \frac{1}{2} \left(\frac{\rho_p^2(0)}{\tilde{S}_0(0)} + \frac{\rho_i^2(0)}{C_0(0)} \right) + \rho_i(0) \ln(\rho_i(0)) + \frac{1}{2} V_{\text{pp}}(0) \rho_p^2(0) + \frac{1}{2} V_{\text{ii}}(0) \rho_i^2(0) + V_{\text{pi}}(0) \rho_p(0) \rho_i(0) \end{aligned} \quad (10)$$

In deformed systems the first term of the right-hand-side of Eq. (10), which is written in brackets, contains the elastic Free Energy. The second term represents the translational entropy of the counterions and the last three terms are interaction parts. This equation indicates, that neglecting fluctuations the Free Energy is just a sum of an elastic, an entropic and an interaction part $F = F_{\text{el}} - TS_{\text{counter}} + F_{\text{int}}$. This reflects the Flory-Rehner Hypothesis. It shows up only on the limit $\mathbf{k} = 0$. Below we will show that this is not all sufficient. In general fluctuations cannot be neglected. In the present network case fluctuations have a strong effect: they violate the Flory-Rehner Hypothesis and renormalize the Gaussian elasticity. If the Free Energy is calculated without neglecting the fluctuations one has to integrate over all $\rho_p(\mathbf{k})$ and $\rho_i(\mathbf{k})$ by performing the path integrals. Eq. (3) shows that in this case there will be a strong coupling between the elastic and the interaction part of the Free Energy. Even in a Debye-Hückel approximation, i.e. $\rho_p(k > 0) = 0$ this coupling cannot be avoided. In the following sections we show, that in polyelectrolyte networks there is a coupling between the elastic and the interaction part and thus the Flory-Rehner Hypothesis is no longer applicable.

III. SINGLE POLYELECTROLYTE CHAIN

To approach the problem of elasticity in polyelectrolyte networks on a systematic basis we recall the results of the single chain deformation. This section will introduce the mathematical method and - more important - it will be shown that the force - extension relationship is fundamentally changed from what is known in Gaussian and excluded volume chains. The deformation of the end - to end - distance of a Gaussian chain by an external force f is simply described by

$$f = k_B T \frac{r}{l^2 N} \quad (11)$$

where T is the temperature, l the Kuhn length, N the chain length and r the distance of the chain ends. This result can be easily derived from the Gaussian statistics of the ideal chain [15]. Already when excluded volume forces are taken into account eq.(11) is changed in a fundamental way. Excluded volume force change the statistical behavior of the chain, i.e., the size of the chain is given by $R \simeq lN^{3/5}$. Thus the single chain is swollen, and another stretching law is expected. This problem was solved by Pincus [8,20]. The result is briefly quoted. The problem is no longer isotropic and the force has two components, i.e., parallel to the stretching direction and perpendicular to the stretching direction. At low deformation a Hookian deformation behavior is expected, whereas at larger deformations the self avoiding statistics comes into play. In the low deformation regime the result is

$$|\langle \mathbf{r}_{\parallel} \rangle| \sim \langle \mathbf{R}^2 \rangle f \quad (12)$$

and in the limit $f \rightarrow \infty$

$$|\langle \mathbf{r}_{\parallel} \rangle| \sim N f^{1/\nu-1} \quad (13)$$

for the elongation in parallel direction to the force \mathbf{f} . For the perpendicular direction it is found ($f \gg 1$)

$$\langle \mathbf{r}_{\perp}^2 \rangle \sim N f^{1/\nu-2} \quad (14)$$

A similar situation will occur in the case of polyelectrolyte chains. The coupling between elasticity and interactions will become much stronger. The interactions are very strong and pre-stretch the chain to a large extend. Thus it is instructive to study the elastic behavior of single polyelectrolytes.

A. Model

Let us first introduce the standard model which is employed here. Since we restrict ourselves to flexible chains which are weakly charged the Edwards model [21] is the appropriate tool, like already given in section II. Here we consider a Debye-Hückel chain, thus neglecting fluctuations of the counterions:

$$\begin{aligned} \beta H_E[\mathbf{r}; \mathbf{f}] = & \frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 + \beta \int_0^{N_0} ds \mathbf{f} \frac{d\mathbf{r}}{ds} \\ & + \frac{bz^2}{2} \int_0^{N_0} ds \int_0^{N_0} ds' \frac{\exp \{ -\kappa |\mathbf{r}(s) - \mathbf{r}(s')| \}}{|\mathbf{r}(s) - \mathbf{r}(s')|}, \end{aligned} \quad (15)$$

where $b = e^2/4\pi\epsilon_0\epsilon_r k_B T$ is the Bjerrum-length, e is the electrical charge of an electron, ϵ_0 is the dielectric constant and ϵ_r the relative dielectric constant. \mathbf{f} is the external force and κ^{-1} denotes the Debye-Hückel screening length. The correlation function can be calculated in terms of a path integral [21–23] as follows:

$$G(\mathbf{r}, N_0; \mathbf{f}) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(N_0)=\mathbf{r}} \mathcal{D}\mathbf{r}(s) \exp \{ -\beta H_E[\mathbf{r}; \mathbf{f}] \}. \quad (16)$$

Its Fourier transform is defined by

$$G(\mathbf{k}, N_0; \mathbf{f}) = \int d^3\mathbf{r} \exp \{ -i\mathbf{k}\mathbf{r} \} G(\mathbf{r}, N_0; \mathbf{f}). \quad (17)$$

The averages of the force-size relationship $\langle \mathbf{R}_{\parallel}^2 \rangle$ and $\langle \mathbf{R}_{\perp}^2 \rangle$, where \mathbf{R}_{\parallel} denotes the parallel component with respect to \mathbf{f} and \mathbf{R}_{\perp} is the corresponding perpendicular part, are then readily calculated by the general formulae

$$\langle \mathbf{R}_{\parallel}^2 \rangle[\mathbf{f}] = - \left. \frac{\partial^2 / \partial k_3^2 G(\mathbf{k}, N_0; \mathbf{f})}{G(\mathbf{k}, N_0; \mathbf{f})} \right|_{\mathbf{k}=\mathbf{0}} \quad (18)$$

and

$$\langle \mathbf{R}_{\perp}^2 \rangle[\mathbf{f}] = - \left. \frac{\sum_{i=1}^2 \partial^2 / \partial k_i^2 G(\mathbf{k}, N_0; \mathbf{f})}{G(\mathbf{k}, N_0; \mathbf{f})} \right|_{\mathbf{k}=\mathbf{0}}. \quad (19)$$

By analytic continuation of the Fourier space to the complex plane, the correlation function $G(\mathbf{k}, N_0; \mathbf{f})$ can also be written as the zero-force correlation function $G(\mathbf{k} - i\beta\mathbf{f}, N_0; \mathbf{f} = \mathbf{0})$. Substitution of Eq. 16 into Eq. 17 yields:

$$G(\mathbf{k}, N_0; \mathbf{f}) = \int d^3\mathbf{r} \exp\{-i\mathbf{k}\mathbf{r}\} \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(N_0)=\mathbf{r}} \mathcal{D}\mathbf{r}(s) \exp\{-\beta H_E[\mathbf{r}; \mathbf{f}]\} \quad (20)$$

For constant force \mathbf{f} Eq. (20) can be rewritten as:

$$\begin{aligned} G(\mathbf{k}, N_0; \mathbf{f}) &= \int d^3\mathbf{r} \exp\{-i(\mathbf{k} - i\beta\mathbf{f})\mathbf{r}\} \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(N_0)=\mathbf{r}} \mathcal{D}\mathbf{r}(s) \exp\{-\beta H_E[\mathbf{r}; \mathbf{f} = \mathbf{0}]\} \\ &= G(\mathbf{k} - i\beta\mathbf{f}, N_0; \mathbf{f} = \mathbf{0}) \end{aligned} \quad (21)$$

Consequently, to get results for $\langle \mathbf{R}_{\parallel}^2 \rangle$ and $\langle \mathbf{R}_{\perp}^2 \rangle$, we only have to calculate $G(\mathbf{k}, N_0)$ and continue the first argument of G to the complex plane.

B. Calculation of the Correlation Function

For technical reasons it is convenient to introduce a field theory, which enables to carry out the variational technique. Thus the field theoretical Hamiltonian reads [16]:

$$\begin{aligned} \beta H[\vec{\psi}] &= \frac{1}{2} \int_{\mathbf{k}} \vec{\psi}(-\mathbf{k}) \left[\mu_0 + \frac{l^2}{6} k^2 \right] \vec{\psi}(\mathbf{k}) \\ &+ \frac{(2\pi)^3}{8} \int_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} \vec{\psi}(\mathbf{k}_1) \vec{\psi}(\mathbf{k}_2) U(\mathbf{k}_1 + \mathbf{k}_2) \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4) \vec{\psi}(\mathbf{k}_3) \vec{\psi}(\mathbf{k}_4) \end{aligned} \quad (22)$$

where $\int_{\mathbf{k}}$ is an abbreviation for $\int d^3\mathbf{k}/(2\pi)^3$ and U denotes the Debye-Hückel potential in units of β^{-1} . In the Fourier space $\tilde{G}(\mathbf{k}, \mu_0)$, which is the Laplace transform of $G(\mathbf{k}, N_0)$ with respect to N_0 , can be written exactly as [24]:

$$\tilde{G}(\mathbf{k}, \mu_0) = \left(\mu_0 + \frac{l^2}{6} k^2 + \Sigma(\mathbf{k}) \right)^{-1} \quad (23)$$

where $\Sigma(\mathbf{k})$ denotes the proper self energy. We now define a trial-Hamiltonian \mathcal{H} :

$$\beta \mathcal{H}[\vec{\psi}] = \frac{1}{2} \int_{\mathbf{k}} \vec{\psi}(-\mathbf{k}) \tilde{\mathcal{G}}^{-1}(\mathbf{k}, \mu_0) \vec{\psi}(\mathbf{k}) \quad (24)$$

where $\tilde{\mathcal{G}}(\mathbf{k}, \mu_0)$ is an approximate correlation function with an approximate proper self-energy $\mathcal{M}(\mathbf{k})$:

$$\tilde{\mathcal{G}}(\mathbf{k}, \mu_0) = \left(\mu_0 + \frac{l^2}{6} k^2 + \mathcal{M}(\mathbf{k}) \right)^{-1}. \quad (25)$$

In this notation the well-known Feynman inequality is given by:

$$F \leq \mathcal{F} + \langle H - \mathcal{H} \rangle_{\mathcal{H}} \quad (26)$$

where

$$\langle \dots \rangle_{\mathcal{H}} = \lim_{n \rightarrow 0} \frac{\int \mathcal{D}\vec{\psi} \dots \exp\{-\beta \mathcal{H}\}}{\int \mathcal{D}\vec{\psi} \exp\{-\beta \mathcal{H}\}} \quad (27)$$

is the mean-value and \mathcal{F} the free energy with respect to \mathcal{H} . The right hand side of the inequality (26) has to be minimized with respect to \mathcal{M} , which is our variational function. The general minimization condition reads

$$\frac{\delta}{\delta \mathcal{M}(\mathbf{q})}(\mathcal{F} + \langle H - \mathcal{H} \rangle_{\mathcal{H}}) = 0 \quad (28)$$

where $\delta/\delta \mathcal{M}(\mathbf{q})$ denotes the functional derivative with respect to $\mathcal{M}(\mathbf{q})$. This condition (28) is equivalent to [16]

$$\begin{aligned} \mathcal{M}(\mathbf{q}) = & \frac{2\pi b z^2 n}{\kappa^2} \int_{\mathbf{k}} \frac{1}{\mu_0 + \frac{l^2}{6} k^2 + \mathcal{M}(\mathbf{k})} \\ & + 4\pi b z^2 \int_{\mathbf{k}} \frac{1}{(\kappa^2 + (\mathbf{q} + \mathbf{k})^2) (\mu_0 + \frac{l^2}{6} k^2 + \mathcal{M}(\mathbf{k}))} \end{aligned} \quad (29)$$

This is a non-linear integral equation for $\mathcal{M}(\mathbf{q})$, which in the following has to be solved approximately, since the exact solution is unknown. At this point it should be stressed, that Eq. (29) represents the well known Hartree approximation. As our aim is to get a force-size relationship according to Eqs. (18) and (19) the ansatz for the approximate proper self energy

$$\mathcal{M}(\mathbf{q}) = \mathcal{M}(\mathbf{0}) + \alpha \mathbf{k}^2 + \mathcal{O}(\mathbf{k}^4) \quad (30)$$

is valid for small external forces f . The constant $\mathcal{M}(\mathbf{0})$ is absorbed by the shifted chemical potential $\mu = \mu_0 + \mathcal{M}(\mathbf{0})$. Consequently the only task is to calculate the coefficient α self-consistently from Eq. (29). This is possible for small inverse screening length κ , which means in the long ranged limit of the Debye-Hückel potential. The result is:

$$\alpha = \frac{2bz^2}{3\pi\mu\kappa} \left[1 + \mathcal{O}\left(\frac{\kappa l}{\sqrt{\mu}}\right) \right] \quad (31)$$

For details see [16].

C. Results

Let us describe the consequences briefly. Inserting the approximate result for the proper self-energy $\Sigma(\mathbf{k})$ into Eq. (44) yields an explicit expression for the correlation function $\tilde{G}(\mathbf{k}, \mu)$ with the shifted chemical potential μ as mentioned above

$$\tilde{G}(\mathbf{k}, \mu) = \left(\mu + \frac{l^2}{6} k^2 + \frac{2bz^2}{3\pi\mu\kappa} k^2 \right)^{-1} \quad (32)$$

Now the conformational free energy of the chain under the influence of a force \mathbf{f} can be calculated very easily by $\phi(\mu, \mathbf{f}) = -\ln \tilde{G}(\mathbf{0}, \mu; \mathbf{f}) = -\ln \tilde{G}(-i\beta\mathbf{f}, \mu)$. Using the well-known thermodynamic relationship

$$N = \frac{\partial \phi(\mu, \mathbf{f})}{\partial \mu} = -\frac{\partial \ln \tilde{G}(-i\beta\mathbf{f}, \mu)}{\partial \mu} \quad (33)$$

we express μ depending on its conjugate variable N and the force \mathbf{f} . Note that the variable N is not the bare number of monomers N_0 since μ is a shifted chemical potential, but N is proportional to N_0 , indeed it is easily seen that $N < N_0$. Considering only singular terms in κ and neglecting terms of order f^4 this calculation yields:

$$\mu = \frac{1}{N} + \frac{4Nbz^2\beta^2 f^2}{3\pi\kappa} + \mathcal{O}(f^4) \quad (34)$$

Substituting Eq. (34) into Eq. (32) we get $G(\mathbf{k}, N)$. According to Eqs. (18) and (19) $\langle \mathbf{R}_{\parallel}^2 \rangle$ and $\langle \mathbf{R}_{\perp}^2 \rangle$ can be calculated from Eq. (33). Expanding in a power series for small forces to second order and again considering only most singular terms for small κ , $\langle \mathbf{R}_{\parallel}^2 \rangle$ becomes for $\beta f/\kappa < 1$

$$\langle \mathbf{R}_{\parallel}^2 \rangle[f] = \frac{4N^2bz^2}{3\pi\kappa} + \beta^2 f^2 \frac{8N^4b^2z^4}{9\pi^2\kappa^2} + \mathcal{O}\left(\frac{\beta^4 f^4}{\kappa^4}\right) \quad (35)$$

The square root of the mean square elongation can be written according to Eq. (35) as

$$\sqrt{\langle \mathbf{R}_{\parallel}^2 \rangle[f] - \langle \mathbf{R}_{\parallel}^2 \rangle[0]} \sim f \quad (36)$$

which is a Hook-like law.

Using the same approximation as mentioned above the root mean square end-to-end distance perpendicular to the force f , $\sqrt{\langle \mathbf{R}_{\perp}^2 \rangle}$, decreases with f for $\beta f/\kappa < 1$, which is contrary to a Gaussian chain [8]. In particular:

$$\langle \mathbf{R}_{\perp}^2 \rangle[f] = \frac{8N^2bz^2}{3\pi\kappa} - \beta^2 f^2 \frac{16N^4b^2z^4}{3\pi^2\kappa^2} + \mathcal{O}\left(\frac{\beta^4 f^4}{\kappa^4}\right) \quad (37)$$

For $f = 0$ the perpendicular end-to-end distance squared becomes doubles exactly $\langle \mathbf{R}_{\parallel}^2 \rangle[0]$, since we have assumed rotational isotropy.

The latter relation ship for zero forces does not agree with one of the two scaling limits, i.e., strong polyelectrolyte regime or excluded volume regime (large κ). In the strong polyelectrolyte regime, very small κ the chain size does not depend on the screening parameter [14], whereas here it does. The reason is that we are here in the intermediate regime where $1/\kappa$ is of the same order as the chain size. This is visible by a detailed study of the renormalization in the chain length from N_0 to N . It is exactly this regime which we need to study the statistical mechanics of networks.

IV. POLYELECTROLYTE NETWORKS

In this section we calculate the modulus of a polyelectrolyte network with a random crosslink configuration.

A. Model

A network is formed out of a very long chain by the instantaneous introduction of a sufficiently large number of crosslinks in the liquid phase (see for example [19]). We restrict ourselves to a network, which consists of flexible, weakly charged strands. Consequently the Edwards model is an appropriate tool to describe the network [21]. Therefore the underlying Hamiltonian is the same as for the single chain Eq. (15). Again we assume Debye-Hückel interaction between the monomers. For the introduction of crosslinks we choose the standard way suggested by Deam and Edwards [18]. We assume for mathematical convenience four functional crosslinks which join two arbitrary segments $\mathbf{r}(s_i)$ and $\mathbf{r}(s_j)$ along the chain. Of course, the value for the free energy then depends on the specific choice of the pairs of monomers, but on macroscopic scale only the statistical average on any crosslink configuration is of importance. Nevertheless this requires non - Gibbsian statistical mechanics in the sense that the crosslink positions represent quenched degrees of freedom.

To calculate therefore the free energy F of the network, we have to take the statistical average over all crosslink configurations \mathbf{S} . This represents the fact, that F is a self averaging quantity.

$$F(N_{\text{tot}}, N_c) = -k_B T \int d\mathbf{S} \mathcal{P}(\mathbf{S}) \ln Z(\mathbf{S}). \quad (38)$$

$Z(\mathbf{S})$ is the constrained partition function for a network with the crosslink configuration \mathbf{S} (see section II), N_c is the number of crosslinks and $\mathcal{P}(\mathbf{S})$ is the crosslink distribution function. Since we assume that the crosslinks are instantaneously introduced in the liquid phase, $\mathcal{P}(\mathbf{S})$ is yielded by the constrained partition function of the liquid phase $Z^{(0)}(\mathbf{S})$ Eq. (1). The crosslink distribution function $\mathcal{P}(\mathbf{S})$ is simply:

$$\mathcal{P}(\mathbf{S}) = \frac{Z^{(0)}(\mathbf{S})}{\int d\mathbf{S}' Z^{(0)}(\mathbf{S}')} . \quad (39)$$

In the following it appears to be reasonable to assume that the so chosen distribution function does not depend on the specific deformation of the network. Note that $Z(\mathbf{S})$ differs generally from $Z^{(0)}(\mathbf{S})$. Since we are interested in deformations of the network, $Z(\mathbf{S})$ is the partition function of the deformed network.

To calculate the free energy F (Eq. (38)) explicitly it is convenient to use of the so called replica trick [18]. Define

$$F_m(N_{\text{tot}}, N_c) = -k_B T \ln \int d\mathbf{S} Z^{(0)}(\mathbf{S}) Z^m(\mathbf{S}), \quad (40)$$

where m is the Replica index. The free energy F , which is averaged over the disorder of the crosslinks, reads [18]:

$$F(N_{\text{tot}}, N_c) = \left. \frac{dF_m(N_{\text{tot}}, N_c)}{dm} \right|_{m=0} \quad (41)$$

As in the case of the single chain, the free energy F is calculated by making use of its relation to the corresponding distribution functions and Green functions of the corresponding propagator (see [16] for the technical details).

B. Field-theoretical Formulation and Results

As in the case of the single chain the external force acts on the ends of the chain and is reintroduced by the analytic continuation to the complex plane:

$$\tilde{G}(\hat{\mathbf{k}}, \mu_0, z_c, \mathbf{f}) = \tilde{G}(\mathbf{k}^{(0)}, \mathbf{k}^{(1)} - i\beta\mathbf{f}, \dots, \mathbf{k}^{(m)} - i\beta\mathbf{f}, \mu, z_c, \mathbf{f} = \mathbf{0}) \quad (42)$$

Here $\tilde{G}(\hat{\mathbf{k}}, \mu_0, z_c, \mathbf{f})$ is the Greens-function, where $\hat{\mathbf{k}}$ is the wave vector in the $3(m+1)$ -dimensional Fourier transformed replica space and $\mathbf{k}^{(i)}$ is the three-dimensional wave vector of the i -th replica, μ_0 is the chemical potential of the monomers and z_c is the fugacity of the crosslinks. To calculate the Greens function $\tilde{G}(\hat{\mathbf{k}}, \mu_0, z_c)$ we introduce a field theory. The field theoretical forceless Hamiltonian for the network in Fourier space reads [19], [16]:

$$\begin{aligned} H[\vec{\psi}(\hat{\mathbf{q}})] = & \int_{\hat{\mathbf{q}}} \left[\frac{\mu}{2} \vec{\psi}(\hat{\mathbf{q}}) \vec{\psi}(-\hat{\mathbf{q}}) + \frac{l^2}{2} \hat{\mathbf{q}}^2 \vec{\psi}(\hat{\mathbf{q}}) \vec{\psi}(-\hat{\mathbf{q}}) \right] \\ & - \frac{z_c}{8} \int_{\hat{\mathbf{q}}_1, \hat{\mathbf{q}}_2, \hat{\mathbf{q}}_3, \hat{\mathbf{q}}_4} \vec{\psi}(\hat{\mathbf{q}}_1) \vec{\psi}(\hat{\mathbf{q}}_2) \vec{\psi}(\hat{\mathbf{q}}_3) \vec{\psi}(\hat{\mathbf{q}}_4) \delta(\hat{\mathbf{q}}_1 + \hat{\mathbf{q}}_2 + \hat{\mathbf{q}}_3 + \hat{\mathbf{q}}_4) \\ & + \sum_{k=0}^m \left[\int_{\hat{\mathbf{q}}_1, \hat{\mathbf{q}}_2} \vec{\psi}(\hat{\mathbf{q}}_1) \vec{\psi}(\hat{\mathbf{q}}_2) \prod_{l \neq k} \delta(\mathbf{q}_1^{(l)} + \mathbf{q}_2^{(l)}) \right] \\ & \times \left[\int_{\hat{\mathbf{q}}_3, \hat{\mathbf{q}}_4} \vec{\psi}(\hat{\mathbf{q}}_3) \vec{\psi}(\hat{\mathbf{q}}_4) \prod_{l \neq k} \delta(\mathbf{q}_3^{(l)} + \mathbf{q}_4^{(l)}) \right] V^{(k)}(\mathbf{q}_3^{(k)} + \mathbf{q}_4^{(k)}) \delta(\mathbf{q}_1^{(k)} + \mathbf{q}_2^{(k)} + \mathbf{q}_3^{(k)} + \mathbf{q}_4^{(k)}) \end{aligned} \quad (43)$$

where $V^{(k)}(q)$ is the Fourier transform of the Debye-Hückel potential in the k -th replica and $\vec{\psi}$ an n -component vector field. The further procedure of the calculation is exactly analogous to the calculation concerning the single chain presented above. Again we introduce a Gaussian trial Hamiltonian with the correlation function:

$$\tilde{\mathcal{G}}(\hat{\mathbf{k}}, \mu_0, z_c) = \left(\mu_0 + \frac{l^2}{6} \hat{k}^2 + \mathcal{M}(\hat{\mathbf{k}}, z_c) \right)^{-1} \quad (44)$$

Then we make use of Feynman's inequality for a variational principle. The variational parameter again is the approximate proper self energy $\mathcal{M}(\hat{\mathbf{k}}, z_c)$. The only difference is, that now the proper self energy depends on a **replicated** Fourier vector $\hat{\mathbf{k}}$. For details see [17]. Assuming a replica symmetry this procedure leads to the following self-consistent equation for $M(\hat{\mathbf{k}}, z_c)$

$$\begin{aligned} M(\hat{\mathbf{k}}, z_c) = & \frac{2\pi b z^2 n(m+1) V_0^m}{\kappa^2} \int_{\hat{\mathbf{q}}} \frac{1}{\mu + \frac{l^2}{6} \hat{\mathbf{q}}^2 + M(\hat{\mathbf{q}}, z_c)} \\ & + 4\pi b z^2 \int_{\mathbf{q}^{(0)}} \frac{1}{(\mathbf{q}^{(0)} + \mathbf{k}^{(0)})^2 + \kappa^2} \frac{1}{\mu + \frac{l^2}{6} (\mathbf{q}^{(0)}, \mathbf{k}^{(1\dots m)})^2 + M(\mathbf{q}^{(0)}, \mathbf{k}^{(1\dots m)})} \\ & + 4\pi b z^2 m \int_{\mathbf{q}^{(1)}} \frac{1}{(\mathbf{q}^{(1)} + \mathbf{k}^{(1)})^2 + \kappa^2} \frac{1}{\mu + \frac{l^2}{6} (\mathbf{k}^{(0)}, \mathbf{q}^{(1)}, \mathbf{k}^{(2\dots m)})^2 + M(\mathbf{k}^{(0)}, \mathbf{q}^{(1)}, \mathbf{k}^{(2\dots m)})} \\ & + \frac{z_c}{2} (n+2) \int_{\hat{\mathbf{q}}} \frac{1}{\mu + \frac{l^2}{6} \hat{\mathbf{q}}^2 + M(\hat{\mathbf{q}}, z_c)}, \end{aligned} \quad (45)$$

where $\mathbf{k}^{(i\dots m)} = (\mathbf{k}^{(i)}, \dots, \mathbf{k}^{(m)})$. This equation has to be solved approximately. In analogy to the calculations on the single chain [16] we restrict ourselves to small external forces applied on the ends of the crosslinked chain. Therefore

we make the same ansatz for the proper-self energy as in the case of the single chain. The only difference is that the proper self energy in this paper is a function depending on the replica-space wave vector $\hat{\mathbf{q}}$:

$$M(\hat{\mathbf{q}}) = a_0 + a_1 \hat{\mathbf{q}}^2 + \mathcal{O}(\hat{\mathbf{q}}^4) \quad (46)$$

In the limit of a weakly charged network and in the long ranged limit of the Debye-Hückel potential the result of the self-consistency calculation according to Eq. (45) for a_0 and a_1 is (for details see [17]):

$$a_1 = \frac{2bz^2}{3l^2\pi\mu_r\kappa} \left[1 + \mathcal{O}\left(\frac{\kappa l}{\sqrt{\mu_r}}\right) \right] \quad (47)$$

and

$$a_0 = \frac{\kappa}{\mu} \left(\frac{2bz^2(m+1)}{\pi} - \frac{bz^2(m+1)}{2} + \frac{2\kappa^2 l^2 bz^2(m+1)}{9\mu\pi} - \frac{\kappa^2 l^2 bz^2(m+1)}{12\mu} \right) - \frac{\kappa}{\mu} \left(\frac{2\kappa^2 z_c m}{3\pi^2} - \frac{\kappa^2 z_c \gamma m}{4\pi^2} - \frac{\kappa^2 z_c \ln(\kappa l / \sqrt{\pi}) m}{2\pi^2} - \frac{\kappa^2 z_c}{6\pi^2} \right) \quad (48)$$

Therefore the approximate Greens function reads:

$$\tilde{\mathcal{G}}(\hat{\mathbf{k}}, \mu, z_c) = \frac{1}{\mu + a_0 + \frac{l^2}{6} \hat{\mathbf{k}}^2 + a_1 \hat{\mathbf{k}}^2} \quad (49)$$

From Eq. (49) the grand canonical partition function in replica space under the influence of an external constant force f acting on the ends of the chain can be calculated:

$$\begin{aligned} \Xi_m(\mu, z_c, \mathbf{f}) &= \tilde{\mathcal{G}}(\mathbf{k}^{(0)}, \mathbf{k}^{(1)} - i\beta\mathbf{f}, \dots, \mathbf{k}^{(m)} - i\beta\mathbf{f}, \mu, z_c)|_{\hat{\mathbf{k}}=\mathbf{0}} \\ &= \frac{1}{\mu + a_0 - \frac{l^2}{6} m\beta^2 \mathbf{f}^2 - a_1 m\beta^2 \mathbf{f}^2} \end{aligned} \quad (50)$$

Here we reintroduced the force f according to Eq. (42). The monomer chemical potential and the fugacity of cross-links which parameterize the grand canonical partition function in Eq. (50), should be expressed in terms of the parameters N_{tot} and N_c . According to Panyukov and Rabin [19] the expression $F_m(N_{\text{tot}}, N_c)$ can be calculated by the method of steepest descent in the thermodynamic limit $N_{\text{tot}}, N_c \rightarrow \infty$:

$$F_m(N_{\text{tot}}, N_c)/k_B T = -\ln \Xi(\mu, z_c) - N_{\text{tot}}\mu + N_c \ln z_c \quad (51)$$

Consequently the fugacity z_c of cross-links and the chemical potential μ of monomers can be obtained by minimizing the right-hand side of Eq. (51):

$$N_{\text{tot}} = -\frac{\partial \ln \Xi_{m=0}(\mu, z_c)}{\partial \mu} \quad (52)$$

and

$$N_c = \frac{\partial \ln \Xi_{m=0}(\mu, z_c)}{\partial \ln z_c} \quad (53)$$

in the limit of a vanishing replica index m . In the weakly charged limit of the network and in the long-ranged limit of the Debye-Hückel potential the result for μ and z_c is:

$$\mu = \bar{N} \quad (54)$$

and

$$z_c = \frac{6\pi^2 \bar{N}^2}{\kappa^3} + \frac{3\pi(4-\pi)bz^2}{\kappa^2} \quad (55)$$

Moreover it can be shown [19], that the conformational free energy of the network is given by:

$$F(N_{\text{tot}}, N_c, f) = -k_B T \left. \frac{\partial \ln \Xi_m(\mu, z_c)}{\partial m} \right|_{m=0} \quad (56)$$

If the free energy F is known the force-size relationship is simply calculated by the derivative of F with respect to the external force f :

$$\langle R \rangle = - \frac{\partial F(N_{\text{tot}}, N_c, f)}{\partial f} \quad (57)$$

After having inserted the results for z_c and μ in the force size relationship, expanded for small charges z neglecting terms of order z^4 and higher, since only weakly charged networks are stable, and considered only terms of leading order with respect to small κ the force-size relationship reads:

$$\langle R \rangle = \left(\frac{bz^2}{3\bar{N}^2\pi\kappa} + \frac{l^2}{6\bar{N}} \right) \beta f + \mathcal{O}(z^4, \kappa) \quad (58)$$

This is again the result for the small deformation regime. The result describes a Hookian law for the force extension relation and defines the elastic modulus of the polyelectrolyte network. Note further that this result is valid for small forces, i.e. $\beta f/\kappa < 1$. Therefore the modulus for the small screening and the low deformation regime of the network reads:

$$G = \left(\frac{\beta bz^2}{3\bar{N}^2\pi\kappa} + \frac{\beta l^2}{6\bar{N}} \right)^{-1} \quad (59)$$

The modulus depends on the density of the crosslink and on the Debye screening parameter. Thus both contributions enter in a significant way. Most important is that part of the modulus stemming from the interactions depends on the crosslink density \bar{N} squared. This now indicates that in the case of strongly interacting soft materials the FRH is no longer applicable. The modulus computed here is a strong combination of both contributions. Moreover we stress that the result is beyond perturbation theory and RPA - type approximations in contrast to earlier suggestions published previously [25]. The author in this paper suggests a modulus which is not changed by the interactions.

V. SWELLING BEHAVIOR

Let us finally discuss the consequences of the above results to the swelling behavior of a simple polyelectrolyte network. The general theory of swelling for these systems is not simple and will be studied in a subsequent publication. Nevertheless we have a good basis to study the general swelling behavior of polyelectrolyte networks. To do so we assume that the equilibrium swelling is given by the c^* - network [8]. The consequence of this assumption is that the single chain behavior can be used for the determination of the degree of swelling. Thus we may restrict ourselves on one mesh of the network, and we can use the single chain behavior studied in the first section of the paper. Of course, we have to neglect complications by the presence of entanglements and topological restrictions. Therefore we can apply the following results only for mesh sizes below typical entanglement lengths. The strong electrostatic repulsion, however, does not allow for a large degree of topological restrictions, which makes the assumption of no entanglements reasonable. To estimate the equilibrium degree of swelling, we use an ideal c^* - network whose monodisperse meshes consist of chains with N monomers. These chains are connected by the process of endlinking, where the functionality of an end of the chain should be six in three dimensions. Thus in the ideal totally stretched state of the network the end-links are on the lattice points of a simple cubic lattice with the lattice constant Nl . Figure 1 shows such a swollen network in two dimensions.

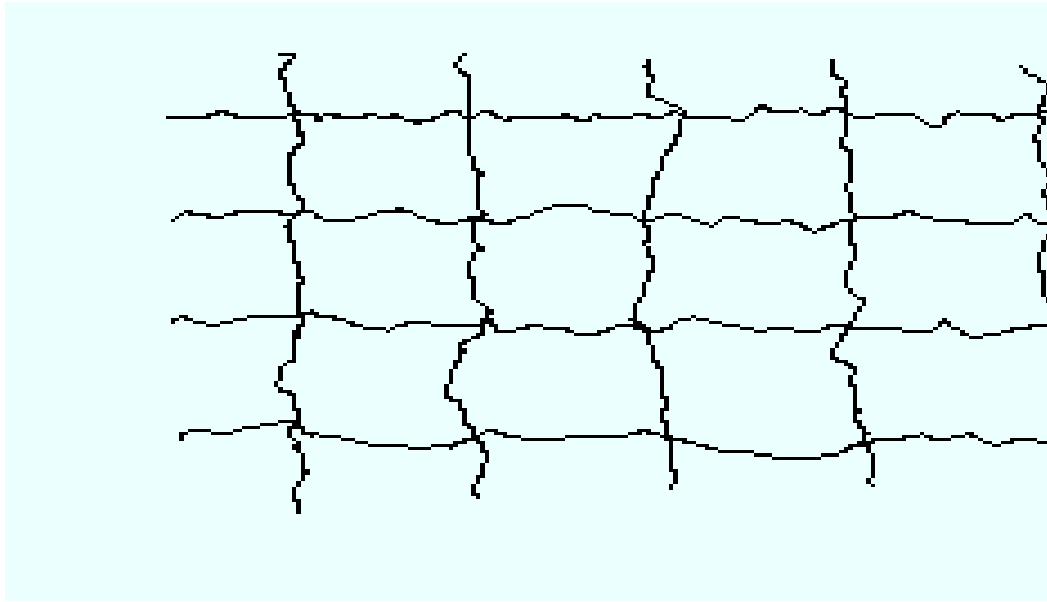


FIG. 1. Swollen network in two dimensions

For long chains this ideal network is of course not very realistic. On the one hand entanglements occur, which disturb the ideal structure drastically. On the other hand two points of the network could be connected, which would be in the ideal, swollen state far away from each other. If the network, however, is synthesized out of short chains, that means N is small, then these defects should occur with a much smaller probability. Consequently in this section we have to restrict ourselves to networks, which are made of very short chains.

In the dry state without having contact to a solvent the considered network is a dense system of neutral polymers, because counterions are bound to the charges on the polymers. In solvent some counterions dissociate and as a result we get a screened Coulomb interaction between the charges, which swells the network. To describe the swelling of a network correctly, one has to know the complete free energy of all the states between unswollen and swollen. This means that we have to have a theory that is valid for the network from the unswollen to the swollen state. As far as we know such a description does not exist by now, because theoretical considerations are only made in special physical limits. Therefore in this section we use the idea of the c^* - network: we compare the volume of the dry and the swollen state of the above mentioned model-network.

The dry state is a dense system of neutral polymers. which means that the remaining excluded volume interaction is screened [11]. Consequently the average end-to-end distance of such a chain is:

$$\langle R_0^2 \rangle \propto l^2 N \quad (60)$$

We assume that the considered model network is formed in an equilibrium state, where the mean end-to-end distances of the chains obey Eq. (60). In the swollen state the averaged end-to-end distances of the chains connecting two neighboring endlink-points in the network can be calculated from Eqs. (35) and (37). For vanishing external forces f :

$$\langle R^2 \rangle \propto \frac{N^2 b z^2}{\kappa} \quad (61)$$

Thus for our model network we can introduce a parameter of swelling Q defined as $Q = V/V_0$, where V is the volume of the swollen network and V_0 is the volume of the unswollen network:

$$Q = \frac{V}{V_0} = \left(\frac{\langle R^2 \rangle}{\langle R_0^2 \rangle} \right)^{\frac{3}{2}} \propto \frac{b^{3/2} z^3}{\kappa^{3/2} l^3 N^{3/2}} \quad (62)$$

Here $\bar{N} = N_e/N_{\text{tot}}$ is the number of endlinks N_e divided by the total number of monomers N_{tot} , i. e. the endlink-density. In our case $N = 1/\bar{N}$ is the averaged number of monomers per strand.

Here we see clearly that in contrast to neutral networks the degree of swelling Q does not only depend on the crosslink density, but also on the range of the interactions via κ and therefore the ionization. A typical dependence on the different quantities is shown in figure 2.

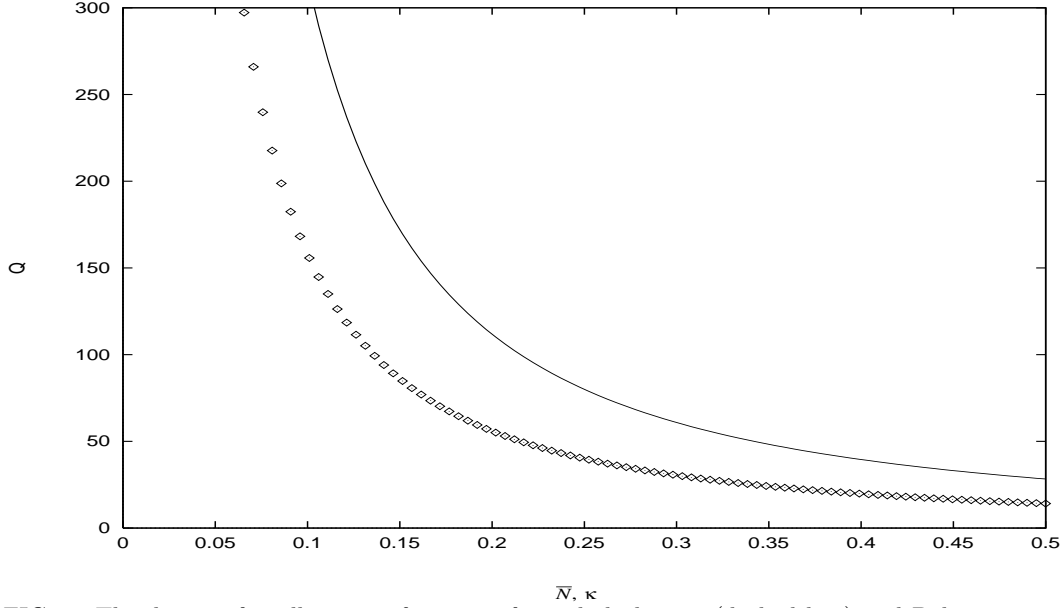


FIG. 2. The degree of swelling as a function of crosslink density (dashed line) and Debye screening parameter (bold-faced line).

VI. DISCUSSION

In this paper we developed different stages of the problem of the elastic behavior of polyelectrolyte networks. This problem required a new approach and the classical theories for neutral networks cannot be used, so far, except in the limit of large salt concentration, i.e., $\kappa \rightarrow \infty$. In this regime the interaction potential between the segments is very short ranged and the network behaves roughly as an "effective excluded volume network". Naturally this regime is not very interesting, since no real new insight can be expected [25]. On the other hand, the small κ regime is very important and novel theories can be formulated [26]. In this regime we found the strong invalidity of the Flory - Rehner - hypothesis, which states that different parts of the free energy can be added. The elastic modulus of the network contains both: the entropic part and the interactions. Both seem to show up as two springs in a series. The equilibrium swelling is determined by interactions and crosslink density.

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APPENDIX A:

Starting from Eq. (2) we introduce the densities $\rho_p(\mathbf{k})$ of the polymers and $\rho_i(\mathbf{k})$ of the counterions. The result is:

$$\begin{aligned}
Z(\rho_p, \rho_i, \mathbf{S}) = & \frac{1}{N_i!} \int \mathcal{D}\mathbf{r}(s) \int \frac{d\mathbf{R}_1}{V_0} \dots \int \frac{d\mathbf{R}_{N_i}}{V_0} \prod_{\mathbf{k}} \delta \left(\rho_p(\mathbf{k}) - \frac{1}{V_0} \int ds e^{i\mathbf{k}\mathbf{r}(s)} \right) \delta \left(\rho_i(\mathbf{k}) - \frac{1}{V_0} \sum_{j=1}^{N_i} e^{i\mathbf{k}\mathbf{R}_j} \right) \\
& \times \exp \left[-\frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 - \ln \left(\prod_{(i,j)} \delta[\mathbf{r}(s_i) - \mathbf{r}(s_j)] \right) - \frac{\beta}{2} \sum_{i,l=1}^{N_i} \frac{bz_i z_l}{\mathbf{k}^2} e^{i\mathbf{k}(\mathbf{R}_i - \mathbf{R}_l)} \right] \\
& \times \exp \left[-\frac{\beta}{2} \int_0^{N_0} ds \int_0^{N_0} ds' \frac{bz^2}{\mathbf{k}^2} e^{i\mathbf{k}(\mathbf{r}(s) - \mathbf{r}(s'))} - \beta \sum_{i=1}^{N_i} \int_0^{N_0} ds \frac{bz_i}{\mathbf{k}^2} e^{i\mathbf{k}(\mathbf{r}(s) - \mathbf{R}_i)} \right] \quad (A1)
\end{aligned}$$

with $b = e^2/4\pi\epsilon_0\epsilon_r k_B T$ the Bjerrum-length. According to the δ -distributions in Eq. (A1) the partition function can be rewritten as:

$$\begin{aligned}
Z(\rho_p, \rho_i, \mathbf{S}) &= \frac{1}{N_i!} \int \mathcal{D}\mathbf{r}(s) \int \frac{d\mathbf{R}_1}{V_0} \dots \int \frac{d\mathbf{R}_{N_i}}{V_0} \prod_{\mathbf{k}} \delta \left(\rho_p(\mathbf{k}) - \frac{1}{V_0} \int_0^{N_0} ds e^{i\mathbf{k}\mathbf{r}(s)} \right) \\
&\times \delta \left(\rho_i(\mathbf{k}) - \frac{1}{V_0} \sum_{j=1}^{N_i} e^{i\mathbf{k}\mathbf{R}_j} \right) \exp \left[-\frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 - \ln \left(\prod_{(i,j)} \delta[\mathbf{r}(s_i) - \mathbf{r}(s_j)] \right) \right] \\
&\times \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} V_{pp}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_p(-\mathbf{k}) - \frac{1}{2} \sum_{\mathbf{k}} V_{ii}(\mathbf{k}) \rho_i(\mathbf{k}) \rho_i(-\mathbf{k}) - \sum_{\mathbf{k}} V_{pi}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_i(-\mathbf{k}) \right]
\end{aligned} \tag{A2}$$

where $V_{pp}(\mathbf{k}) = bz^2/\mathbf{k}^2$. V_{pi} and V_{ii} are defined analogously. The δ -functions in Eq. (A2) can be rewritten by use of a ϕ - and ϕ' -field:

$$\begin{aligned}
Z(\rho_p, \rho_i, \mathbf{S}) &= \frac{1}{N_i!} \int \mathcal{D}\mathbf{r}(s) \int \frac{d\mathbf{R}_1}{V_0} \dots \int \frac{d\mathbf{R}_{N_i}}{V_0} \int \mathcal{D}\phi(\mathbf{k}) \exp \left[i\phi(\mathbf{k}) \left(\rho_p(\mathbf{k}) - \frac{1}{V_0} \int_0^{N_0} ds e^{i\mathbf{k}\mathbf{r}(s)} \right) \right] \\
&\times \int \mathcal{D}\phi'(\mathbf{k}) \exp \left[i\phi'(\mathbf{k}) \left(\rho_i(\mathbf{k}) - \frac{1}{V_0} \sum_{j=1}^{N_i} e^{i\mathbf{k}\mathbf{R}_j} \right) \right] \\
&\times \exp \left[-\frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 - \ln \left(\prod_{(i,j)} \delta[\mathbf{r}(s_i) - \mathbf{r}(s_j)] \right) \right] \\
&\times \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} V_{pp}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_p(-\mathbf{k}) - \frac{1}{2} \sum_{\mathbf{k}} V_{ii}(\mathbf{k}) \rho_i(\mathbf{k}) \rho_i(-\mathbf{k}) - \sum_{\mathbf{k}} V_{pi}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_i(-\mathbf{k}) \right]
\end{aligned} \tag{A3}$$

Within a Gaussian approximation the partition function reads:

$$\begin{aligned}
Z(\rho_p, \rho_i, \mathbf{S}) &= \frac{1}{N_i!} \int \mathcal{D}\mathbf{r}(s) \int \frac{d\mathbf{R}_1}{V_0} \dots \int \frac{d\mathbf{R}_{N_i}}{V_0} \int \mathcal{D}\phi(\mathbf{k}) e^{i\phi(\mathbf{k}) \rho_p(\mathbf{k})} \\
&\times \left(1 - i\phi(\mathbf{k}) \int_0^{N_0} ds e^{i\mathbf{k}\mathbf{r}(s)} - \frac{\phi^2(\mathbf{k})}{2} \int_0^{N_0} ds \int_0^{N_0} ds' e^{i\mathbf{k}(\mathbf{r}(s) - \mathbf{r}(s'))} \right) \\
&\times \int \mathcal{D}\phi'(\mathbf{k}) e^{i\phi'(\mathbf{k}) \rho_i(\mathbf{k})} \left(1 - i\phi'(\mathbf{k}) \sum_{j=1}^{N_i} e^{i\mathbf{k}\mathbf{R}_j} - \frac{\phi'^2(\mathbf{k})}{2} \sum_{j,l=1}^{N_i} e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_l)} \right) \\
&\times \exp \left[-\frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 - \ln \left(\prod_{(i,j)} \delta[\mathbf{r}(s_i) - \mathbf{r}(s_j)] \right) \right] \\
&\times \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} V_{pp}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_p(-\mathbf{k}) - \frac{1}{2} \sum_{\mathbf{k}} V_{ii}(\mathbf{k}) \rho_i(\mathbf{k}) \rho_i(-\mathbf{k}) - \sum_{\mathbf{k}} V_{pi}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_i(-\mathbf{k}) \right]
\end{aligned} \tag{A4}$$

Denote by $\tilde{S}_0(\mathbf{k})$ and $C_0(\mathbf{k})$:

$$\tilde{S}_0(\mathbf{k}) = \left\langle \int_0^{N_0} ds \int_0^{N_0} ds' e^{i\mathbf{k}(\mathbf{r}(s) - \mathbf{r}(s'))} \right\rangle_0 \tag{A5}$$

and

$$C_0(\mathbf{k}) = \left\langle \sum_{j,l=1}^{N_i} e^{i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_l)} \right\rangle_0 \tag{A6}$$

where $\langle \dots \rangle_0$ means the expectation value with respect to H_0 with:

$$\beta H_0 = \frac{3}{2l^2} \int_0^{N_0} ds \left(\frac{d\mathbf{r}}{ds} \right)^2 + \ln \left(\prod_{(i,j)} \delta[\mathbf{r}(s_i) - \mathbf{r}(s_j)] \right) \tag{A7}$$

Line two and three of Eq. (A4) are now replaced by the mean values of the terms concerning H_0 . The result is considered as the first terms of a series expansion of an exponential function. Consequently the exponential function is reintroduced. After having integrated over ϕ and ϕ' the partition function reads [27]:

$$Z(\rho_p, \rho_i, \mathbf{S}) = \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \left(\frac{1}{\tilde{S}_0(\mathbf{k})} + V_{pp}(\mathbf{k}) \right) \rho_p(\mathbf{k}) \rho_p(-\mathbf{k}) \right] \\ \times \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \left(\frac{1}{C_0(\mathbf{k})} + V_{ii}(\mathbf{k}) \right) \rho_i(\mathbf{k}) \rho_i(-\mathbf{k}) - \sum_{\mathbf{k}} V_{pi}(\mathbf{k}) \rho_p(\mathbf{k}) \rho_i(-\mathbf{k}) \right] \quad (\text{A8})$$

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